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(54) Title: CELLULOSE TREATMENT AND THE RESULTING PRODUCT (57) Abstract The invention is a process for preparing a chemical pulp useful for preparation of cellulose derivatives and cellulose fibers. It involves first treating a conventional kraft pulp with an aqueous alkali to swell the fibers. The swollen fibers are then washed and further treated with an enzyme having cellulase activity. Temperature, concentration, and time of enzyme treatment are controlled so that a desired degree of polymerization is reached. Conditions are also controlled so that the pulp preferably remains in the Cellulose I phase during swelling and washing. The swelling and enzyme treatment can be made at any time before, during, or following the bleaching sequence. Endogluconases having a cellulose binding domain portion are preferred. The products of the invention are particularly useful in the manufacture of lyocell fibers.		

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CELLULOSE TREATMENT AND THE RESULTING PRODUCT

This application claims priority from Provisional Application Serial No. 60/060,631, filed October 1, 1997.

5 The present invention is a method for treatment of wood pulp cellulose to increase its suitability for derivitization or use as a raw material for rayon or lyocell production. In particular the process is directed to improvement of the chemical and physical characteristics of cellulose made by the conventional kraft process.

Background of the Invention

10 Probably the earliest use of chemically modified cellulose as a fiber dates back to about 1855 when an artificial silk made from nitrocellulose was patented. The process did not mature until about 1885. Nitrocellulose rayon was manufactured in the United States beginning about 1920 but the product never assumed significant commercial importance. The manufacture of cellulose acetate rayon in America began four
15 years later. The basic process for production of cuprammonium rayon was patented in 1890 and the viscose process was discovered two years later. Much more recently a new generic type of cellulose fibers has become commercially available. Termed lyocell, these are formed of cellulose spun from solution, as are the rayons, but without the formation of any intermediate chemical compounds of cellulose. Lyocell fibers are made
20 from cellulose dissolved in wet N-methylmorpholine-N-oxide. This solution is spun into air, where the latent fibers are drawn to decrease diameter and increase molecular orientation. The fibers are then directed into a nonsolvent, such as water or lower aliphatic alcohols, where the cellulose is regenerated from solution. In contrast, viscose and cuprammonium rayons are spun directly into a regenerating solution and then appropriately drawn. Probably the earliest patent describing the formation of lyocell fibers is
25 U.S. 2,179,181 to Grenacher. U.S. Patent 4,246,221 to McCorsley III appears to be basic to the present commercial process for forming lyocell fibers.

Commercial thermoplastics based on cellulose esters and ethers have been available following the introduction of camphor plasticized cellulose nitrate about 1870.

30 One thing all of the above cellulose products have in common is that they require a relatively highly purified cellulose as a starting material. Initially cotton was used. Later purified cotton linters were found satisfactory. Linters are the short fibers a few millimeters in length that remain attached to the seed after the staple fibers have

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been removed. They are purified by a simple extraction in dilute caustic soda at elevated temperature and pressure followed by bleaching.

Cellulose manufactured by the sulfite process first became available in Sweden in 1874. Until about 1950 only purified cotton linters and sulfite pulps were used for manufacture of cellulose derivatives and fibers. Wood pulp produced by the kraft process was not generally considered suitable because of poor and nonuniform reactivity. This situation changed about 1950 with the advent of prehydrolyzed kraft pulps. With this process the wood chips are given a preliminary acid hydrolysis to remove a large portion of the hemicellulose prior to further purification by standard kraft pulping methods. However, the prehydrolysis step is an option for only a very small number of kraft mills since it then requires batch digesters for further processing. Most kraft mills today are equipped with continuous digesters.

The wood pulps, so called "chemical pulps" or "dissolving pulps", used for the above products usually have about 94-96% alpha cellulose. Cotton linters average about 98% alpha cellulose. Sulfite pulps reach this level by the use of a strong caustic extraction during the bleaching process. As was just noted, an acid prehydrolysis has heretofore been essential to the production of high alpha kraft chemical pulps. Today, in the U.S. and Europe, material insoluble in 18% caustic soda at 25°C, measured by Tappi Method T235, correlates closely and is considered equivalent to alpha cellulose.

Degree of polymerization (DP) of the purified cellulose is another property important to satisfactory production of the different end products and must be controlled accordingly. DP is estimated from the viscosity of a solution of cellulose in aqueous cupric ammonium hydroxide or cupriethylene diamine made under standard conditions. Most cellulose thermoplastics, such as ethyl cellulose or other ethers, require a cellulose with a high DP; e.g., about 2400. Cellulose esters, such as cellulose acetate, normally require a cellulose of about 1500 DP. Pulps intended for production of rayon fibers must usually have a DP of about 1000. This is necessary to enable sufficiently high concentrations of cellulose in the spinning solutions while keeping the solution viscosity adequately low so that extrusion parameters are manageable. In the manufacture of sulfite pulps, a large measure of DP control can be obtained by adjusting the pulping conditions. Similarly, adjustments made in the prehydrolysis stage of kraft chemical pulps can effect DP control.

In contrast to chemical pulps, conventional kraft pulps are normally manufactured by processes that give a high DP pulp with a modest 86-88% alpha cellulose content. Strength and yield are normally paramount properties of kraft pulps. Major markets include paper and packaging products and absorbent products such as disposable diapers. Regular kraft pulps have not found significant use for production of

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cellulose derivatives or fibers. The kraft process is virtually required when the wood supply is predominantly pitchy softwoods, such as Douglas-fir or the southern pines.

The degradation of cellulose by enzymes is well known and has been extensively investigated. The various wood rot fungi employ enzymatic attack as the mechanism that degrades the cellulose to sugars to supply their metabolic needs. Enzymatic saccharification of cellulose has been proposed to produce simple sugars such as glucose or xylose.

The present invention is specifically directed to converting regular kraft process wood pulps, without the need for a prehydrolysis step, into products suitable for the manufacture of cellulose derivatives and fibers. The process is especially useful for mills equipped only with continuous digesters since it can be carried out in standard bleaching equipment.

Summary of the Invention

The present method involves swelling a wood cellulose product and then treating it with a cellulolytic enzyme to reduce and control DP. Swelling increases the accessibility of the cellulose to the action of the enzyme. A preferred enzyme is a cellulase or enzyme with cellulase activity. While a bleached kraft pulp is preferred, the pulp need not be bleached and wood celluloses made by other pulping processes; e.g., sulfite pulps, are believed to be equally suitable. The method can be used at any point after the brownstock washers, either before, after, or during the bleaching sequence. Any of the known cellulose swelling agents are normally satisfactory. These are primarily inorganic and organic alkaline compounds. Exemplary inorganic compounds include Group I metal hydroxides and ammonium hydroxide. Exemplary organic compounds include C₁ to C₄ aliphatic primary amines, ethylene diamine, and diethylene triamine. Many cellulose solvents also act as swelling agents in selected concentrations. An example might be an aqueous solution of N-methylmorpholine-N-oxide (NMMO). Most preferably, the swelling is carried out in a solution of about 8-12% NaOH at elevated temperature, although concentrations as low as 2% have been found effective. The swelling agent is essentially completely removed by washing before the enzyme treatment.

It is preferable during the swelling and subsequent washing steps to avoid conditions which would cause mercerization of the cellulose fibers. Stated otherwise, the cellulose should preferably be treated under conditions that would maintain it in the Cellulose I phase and avoid entry into the Cellulose II phase.

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Alternatively, a second treatment similar to the initial swelling treatment may be carried out following the enzyme treatment. However this does not appear to be critical.

Compounds containing cellulase enzymes are commercially available from a number of suppliers. These are usually produced by culturing various cellulose attacking wood rot fungi or bacteria and subsequently extracting the active enzymes. Cellulase enzymes are also cultured from genetically modified organisms. The preferred enzymes are those usually classified as endoglucanases. Endoglucanases cleave the cellulose molecules away from the ends of the polymer chain and are effective for DP reduction when the cellulose is exposed to them for a limited time. Different products will have various levels of activity and concentrations used will vary depending on an activity assay as well as the particular cellulose substrate being treated. Endoglucanases possessing a cellulose binding domain (CBD) portion on the enzyme molecule are particularly useful.

In addition to the DP control effected by the enzymes, certain alkali soluble portions of the kraft pulp; e.g., hemicelluloses, will be removed by the swelling and subsequent washing step.

Conventional wisdom among cellulose chemists is that a strong acid treatment at some time in the pulping or bleaching sequence is essential for promoting good chemical reactivity. While explanations vary, it is believed that the acid treatment attacks the fiber wall in a manner so that accessibility to reactants is significantly increased and uniformity of reaction is improved. Since such an acid treatment is lacking in conventional kraft processing, the pulps generally have poor and uneven reactivity. Even alkali extraction to increase alpha cellulose fails to achieve a significant improvement. Use of the present process enables conventional kraft pulps to be modified so that they can be successfully used in place of the more specialized dissolving pulps, especially in applications where lower DP pulps are desirable. While the products of the invention are useful for preparation of many types of cellulose derivatives, they are especially well adapted for production of cellulose fibers such as rayons or lyocell.

Pulps suitable for the invention can be either hardwood or softwood types or they may be mixtures of hardwood and softwood fibers. In particular, the process is especially suitable for making dissolving grade material from southern pine kraft pulps without the necessity of using an initial prehydrolysis stage.

It is thus an object of the invention to provide a process whereby a conventional bleached kraft wood pulp can be made suitable for production of cellulose derivatives and cellulose fibers.

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It is a further object to provide a process for production of a chemical grade pulp produced by the kraft process but without the requirement of a preliminary hydrolysis.

It is another object to provide an enzymatic method for control of degree
5 of polymerization of kraft pulps.

These and many other objects will become readily apparent upon reading the following detailed description taken in conjunction with the drawing.

Brief Description of the Drawing

The single figure is a phase diagram showing the boundary between non-
10 mercerizing and mercerizing conditions for cellulose undergoing alkaline treatment.

Detailed Description of the Preferred Embodiments

The cellulose pulp used for the examples described herein was a never dried bleached southern pine kraft market pulp provided by Weyerhaeuser Company, New Bern, North Carolina. In its dried and sheeted form this is sold commercially as
15 Grade NB416. This product and many similar products from other suppliers are widely used for production of fluff for disposable diapers but are also used for manufacture of many different types of office papers and other products.

It can be generalized that cellulase enzymes tend to attack the cellulose molecules while xylanase enzymes selectively hydrolyze the shorter molecular chain xy-
20 lan component of the hemicellulose. Some enzymes exhibit both types of activity. The action of most endogluconase enzymes is believed to be by scission of the cellulose molecules, at mid-molecule so to speak, rather than to attack the ends of the molecules. The presently preferred enzymes are those that exhibit high endogluconase activity.

Enzyme activity is determined by the so-called DNS method described by
25 T. K. Ghose, Measurement of Cellulase Activities, *Pure and Applied Chemistry*, 59 (2): 257-268 (1987). Briefly, a sample of an assay substrate such as cellulose, cellobiose or carboxymethyl cellulose is placed in a container with a sample of the enzyme and a buffer solution giving a pH appropriate to the enzyme being tested. For the present work, a carboxymethyl cellulose designated 7LF has been used as the assay substrate for
30 cellulase activity, ground birchwood xylan as the substrate for xylanase activity, and konjac flour for mannanase activity. The CMC designation indicates a low viscosity product with a degree of substitution of about 0.7. Following a reaction time of 1 hour, reducing sugars present are estimated by colorimetric analysis after addition of dini-trosalicylic acid (DNS) and a brief heating period.

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Example 1

The following procedure was used for all of the treatments that will be subsequently described. Into a suitable container was placed 100 g, dry basis, of the above wood pulp. The amount of water present with the pulp was determined. To this
5 was added caustic soda solution at 70°C. The water present in the pulp sample was considered in making the caustic solution so that a 10% concentration by weight NaOH resulted in the treating solution. Sufficient caustic solution was used to make the consistency about 6%. Total weight of the mixture was about 1667 g with 1567g of 10% NaOH solution. The temperature was maintained at 70°C for 1 hour with gentle stir-
10 ring. Following the swelling treatment the caustic solution was drained and the swollen pulp initially washed with hot water, also at 70°C. Subsequent washes were with ambient temperature water. Washing was continued until the effluent water was at approximately neutral pH.

The initial hot water wash was used to ensure that conditions would not be
15 favorable for formation of Cellulose II during removal of the caustic swelling solution. Reference to the Figure shows a boundary line between Cellulose I and Cellulose II at various caustic concentrations and temperatures.

The swollen cellulose was reslurried in water at 50°C to 5% consistency at neutral pH. The calculated amount of enzyme was then added to give the desired
20 units per gram of cellulose. Either 3, 23, or 30 units/g were used. Enzyme treatment was continued at 50°C with gentle agitation for 2 hours. The treated cellulose was again washed using ambient temperature water. In some cases as noted following, a second caustic treatment similar to the initial treatment was employed after the enzyme treatment. Following washing the treated cellulose was then dried as loose fluff for
25 analysis and testing.

The enzymes used in the experiments to be described are available from Novo Nordisk, Bagsvaerd, Denmark. This is not intended as an endorsement of these particular products since equally suitable products are believed to be available from other suppliers. The following materials were used: Pulpzyme HC -- predominantly a
30 xylanase; Novozym 342 -- a cellulase with significant xylanase activity; SP476 -- an endogluconase with cellulose binding domain (CBD); SP613 -- an endogluconase lacking CBD; and Gamanase -- a mannanase. Assay activities of these enzymes were determined to be as follows as seen in Table 1:

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Table 1
ACTIVITY

	<u>Cellulase</u>	<u>Xylanase</u>	<u>Mannanase</u>
Pulpzyme HC	0	7,900	4
Novozym 342	140	4,200	260
Gamanase	16	19	5,300
SP 476	74	0	11
SP 613	105	15	2,100
Assay substrate	CMC 7LF	birchwood xylan	konjac flour

In the following Table 2, R10 and R18 are determined by Tappi Method T235 and represent respectively the percentage of original sample insoluble in 10% or 18% NaOH at 25°C. The 10% NaOH treatment is believed to extract degraded cellulose and hemicellulose while 18% NaOH extracts mainly hemicellulose. Both correlate with alpha cellulose measured by Tappi Method T203. Xylose and mannose are determined by hydrolysis and are degradation products of hemicellulose. They are indicators of the amount of hemicellulose in the sample.

Table 2
10% NaOH Swell --Enzyme Treatment -- 10% NaOH Extraction

<u>Sample</u>	<u>Enzyme</u>	<u>Dose, Units/g</u>	<u>DP</u>	<u>R10</u>	<u>R18</u>	<u>Xylose</u>	<u>Mannose</u>
1	Starting Material	Untreated	1,252	86.1	86.6	3.8	4.2
2	None	NaOH Only	1,130	97.6	96.7	1.1	4.1
3	Pulpzyme HC	3	1,245	97.4	96.4	1	3.9
4	Pulpzyme HC	30	1,103	97.5	97	0.5	3.2
5	Novozym 342	3	870	93.4	95.6	0.6	3
6	Novozym 342	30	521	90.6	94.8	0.4	2.8
7	HC/342	3/3	800	95.2	96.2	0.3	2.4
8	HC/342	30/30	465	90.5	94.7	0.4	3
9	Gamanase	3	1,113	95.4	95.5	1.6	3.9

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All of the above samples were treated at pH 7 and 50°C with the exception of Gamanase which was at pH 4.8 and 65°C. It is readily apparent from the above data that the xylanase and mannanase are not effective at reducing cellulose DP under the conditions employed. The Novozym 342 effected significant reduction in DP. Mixtures of the Novozym 342 with the xylanase Pulpzyme HC were approximately equal in performance to that of Novozym alone. Samples 5-8, which had the cellulase treatment, show relatively lower R10 values than the others yet have lower extractable sugar content. This is interpreted to mean that the enzymes have produced some shorter cellulose chains which have alkali solubility. It is evident from the high R10 and R18 values of samples having only the alkali swelling treatment (Sample 2) and the alkali swelled xylanase treated samples (Samples 3 and 4) that hemicellulose is effectively removed.

The above work was repeated comparing Novozym 342 to SP 476, an endoglucanase with CBD activity and with SP613, an endoglucanase without CBD activity. Enzyme treatment was at 50°C and pH 7 with caustic treatments before and after the enzyme treatment. Results are seen in Table 3.

Table 3
Comparison of Endoglucanase with and without CBD Activity

Sample	Enzyme	Dose, Units/g	DP	R10	R18	Xylose	Mannose
10	Starting material	Untreated	1,229	86.4	86.7	4.9	6
11	None	NaOH Only	1,330	96.1	95.3	1.5	4.1
12	Novozym 342	3	957	94.3	94.7	0.4	2.5
13	SP476 (with CBD)	3	610	91.1	93.5	0.7	4
14	SP476 (with CBD)	23	520	88.6	93.6	0.8	3.4
15	SP613 (w/o CBD)	3	1,146	96.6	95.9	0.8	4
16	SP613 (w/o CBD)	23	1,043	95.2	95.4	0.7	4.5

The greater effectiveness of the endoglucanase with CBD activity at reducing DP is immediately evident. Once again, even though R18 is somewhat lower compared with the 10% NaOH treatment only, sugars remain lower than the control samples indicating a low hemicellulose content.

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To investigate the effect of a single initial swelling treatment vs treatments before and after the enzyme the following work was done. In all cases the Step 2 enzyme treatment used the mixture of Pulpzyme HC/Novozym 342 at 3/3 units/g as was described in Table 1. Treatment was again at 50°C and pH 7. Results are shown in Table 4.

Table 4
Comparison of Single vs Before and After Caustic Treatment

<u>Sample</u>	<u>Step 1</u>	<u>Step 3</u>	<u>DP</u>	<u>R10</u>	<u>R18</u>	<u>Xylose</u>	<u>Mannose</u>
17	Starting Material	Untreated	1,131	86.5	87.3	8.6	5.9
18	Wash Only	Wash Only	1,041	86	87.4	4.2	5.6
19	Wash Only	10% NaOH/wash	1,313	93.6	93.6	1.9	4.7
20	pH 10 Then Wash	Wash Only	1,024	85.1	87.1	5.6	5.3
21	pH 10 Then Wash	10% NaOH/Wash	1,009	96.7	93.8	2.3	5.4
22	2% NaOH/Wash	Wash Only	943	85.5	86.7	6.9	6.7
23	2% NaOH/Wash	10% NaOH/Wash	1,074	93.1	93.3	0.9	4.8
24	10% NaOH/Wash	Wash Only	719	89.1	92	1.9	4.8
25	10% NaOH/Wash	10% NaOH/Wash	892	93.9	95	1	4.6
26	10% NaOH/Wash*	10% NaOH/Wash	1,198	96.2	95.3	0.9	4
27	10% NaOH/Wash*	None	1,261	94.2	93.7	2	5

* No Step 2 enzyme treatment

Comparing Samples 20-23 with 24 and 25, it is evident that the initial swelling in stronger caustic is critical to DP reduction. Similarly, comparing Samples 22 with 23 and 24 with 25, it becomes evident that the second caustic treatment is not essential for DP reduction. As seen with Samples 26 and 27, caustic treatment alone does not effect any DP reduction.

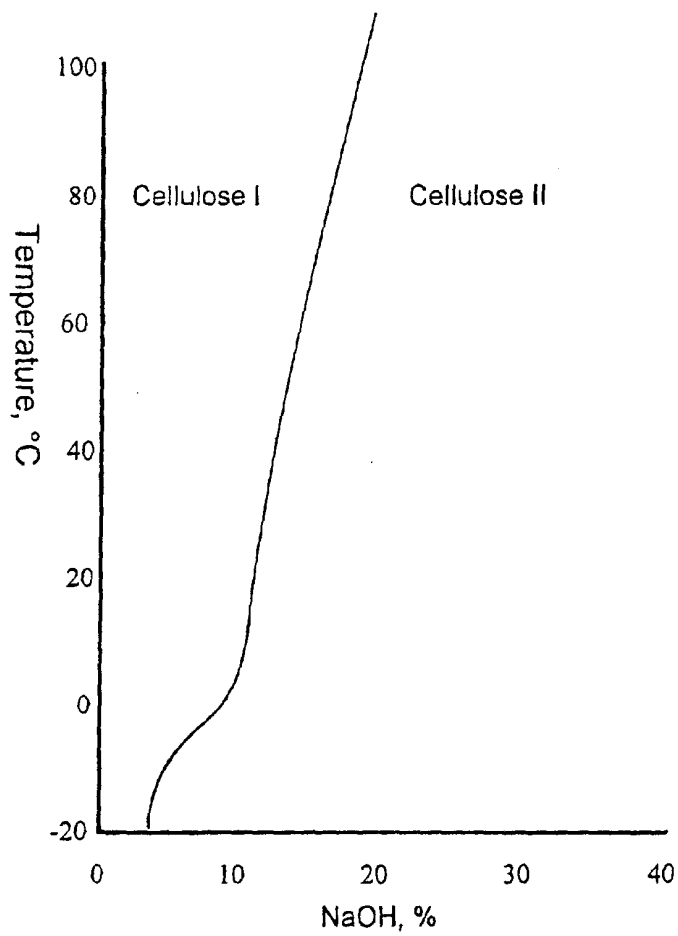
While enzymatic treatment of cellulose with cellulases has been studied before, this has not been used heretofore in conjunction with preliminary swelling for DP control of the product. Nor has this process been used to make a chemical pulp from a conventional kraft pulp. The invention thus resides in an initial swelling of the kraft cellulose followed by a treatment with a cellulase enzyme to effect DP control and to the pulp produced by the process.

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Claims:

1. A method of treating a cellulose pulp product which comprises:
swelling the pulp while in an aqueous suspension;
washing the pulp to remove the swelling agent;
5 treating the swollen pulp with an enzyme having cellulolytic activity for a
sufficient time to effect a desired reduction in degree of polymerization of the cellulose.
2. The method of claim 1 wherein the alkali in the swelling solution is se-
lected from the group consisting of sodium hydroxide, potassium hydroxide, and
ammonia.
- 10 3. The method of claim 1 wherein the enzyme is an endoglucanase.
4. The method of claim 1 in which the endoglucanase possesses a cellulose
binding domain.
5. The method of claim 1 in which temperature and concentration of the
swelling conditions are chosen so as to maintain the pulp in the Cellulose I phase.
- 15 6. The method of claim 5 in which the alkali swollen pulp is initially
washed with water at a temperature sufficiently elevated to ensure that the cellulose re-
mains in the Cellulose I phase.
7. The method of claim 1 in which the alkali in the swelling solution is so-
dium hydroxide and the enzyme is an endoglucanase possessing cellulose binding do-
20 main activity.
8. The method of claim 7 in which the sodium hydroxide concentration is
2-12% and the treatment temperature is higher than 20°C.
9. The method of claim 1 in which the cellulose is a bleached kraft pulp.
10. The method of claim 9 in which the kraft pulp has an initial degree of
25 polymerization in the range of about 1000-1400 and the final degree of polymerization is
in the range of about 400-800.
11. Cellulose prepared by the process of claim 1.

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*Fig. 1*

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 98/20303

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21C9/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9551 Derwent Publications Ltd., London, GB; Class D16, AN 95-401702 XP002089461 & JP 07 279078 A (HONSHU PAPER MFG CO LTD) , 24 October 1995 see abstract	1,9,11
X	EP 0 181 249 A (DU PIN CELLULOSE) 14 May 1986 see page 4, line 22 - line 36; claims; examples 11-14	11
Y		1,2,5,6, 8-10
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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8 January 1999

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

In: tional Application No

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